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(54) MULTI-LAYERED BLOW-MOLDED BOTTLES

(71) We, MITSUI PETROCHEMICAL INDUSTRIES LTD., a Japanese body corporate of 2-5, 3-chome, Kasumigaseki, Chiyoda-ku, Tokyo, Japan, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

10 This invention relates to a multi-layered blow-molded bottle.

Blow-molded bottles made of polyolefins are known but they suffer from such defects as high gas-permeability, attack by organic solvents, lack of rigidity or poor transparency. All of these defects are ascribable to the inherent properties of polyolefins and, in order to make up for the defects, multi-layered bottles have been prepared composed of a polyolefin layer and a layer of another thermoplastic polymer such as polyamide. The multi-layered bottles are usually produced using a blow-molding apparatus including an extrusion device composed of an extrusion die having an annular extrusion orifice and a multiplicity of extruders connected to the die, an air injecting device for blowing the extruded tube into the form of a bottle, and partition molds. The starting polyamide and polyolefin are fed separately into the extruders and extruded towards the die, and then pass through the annular passage in the die. Finally, they are extruded in a two-layered tubular form from the extrusion orifice. The extruded two-layered tube is held between the partition molds and confined therein. Air is injected into the confined tube, and the tube is blown into the form of a bottle. This method of producing multi-layered bottles is described in detail in Japanese Patent Publication No. 23635/69.

40 However, because of poor adhesion between the polyolefin and the polyamide, the layers tend to separate from each other and in as

extreme cases, the bottles so produced have poorer properties than the single layer bottles and are of little commercial value.

The present invention provides a multi-layer blow-molded bottle in which the constituent layers are firmly bonded to each other and which does not suffer the defects of single layer polyolefin bottles.

According to the invention there is provided a bottle comprising at least one layer (1) of a polyamide and at least one layer (2) of a thermoplastic organic polymer composition containing a polyolefin having at least one monomer grafted thereto, the monomer being an ethylenically unsaturated carboxylic acid or an anhydride, ester, amide, imide or metal salt thereof.

Examples of polyolefins which can be used in the present invention are homopolymers of ethylene and propylene, copolymers of ethylene and propylene, copolymers of ethylene and 1-butene, copolymers of ethylene and 1-hexene, and copolymers of propylene and 1-butene.

When polyethylene is used, it should preferably have a melt index (190°C.) of at least 0.02, and when polypropylene is used, it should preferably have a melt index (230°C.) of at least 0.05.

Specific examples of the monomer to be grafted to the polyolefin (to be referred to as a graft monomer hereinafter) include ethylenically unsaturated carboxylic acids such as acrylic acid, methacrylic acid, maleic acid, fumaric acid and itaconic acid; acid anhydrides such as maleic anhydride, acrylic anhydride, methacrylic anhydride and itaconic anhydride; esters such as methyl acrylate, ethyl acrylate, butyl acrylate, glycidyl acrylate, methyl methacrylate, ethyl methacrylate, butyl methacrylate, glycidyl methacrylate, monoethyl maleate, diethyl maleate, monomethyl fumarate, dimethyl fumarate, mono-n-butyl itaconate and di-n-butyl itaconate; amides such as maleic acid monoamide, maleic acid

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diamide, maleic acid-N-monoethylamide, maleic acid-N,N-diethylamide, maleic acid-N-monobutylamide, maleic acid-N,N-dibutylamide, fumaric acid monoamide, fumaric acid diamide, fumaric acid-N,N-diethylamide, fumaric acid-N-monobutylamide and fumaric acid-N,N-dibutylamide; imides such as maleimide N-butyl maleimide and N-phenyl maleimide; and metal salts such as sodium acrylate, potassium methacrylate. Of these, maleic anhydride and acrylic acid are preferred.

The grafting of an unsaturated carboxylic acid or a derivative thereof to a polyolefin is known. For example, Japanese Patent Publication No. 6384/64 describes the details of a method of mixing a polyolefin, a graft monomer and a catalyst simultaneously, and melting the mixture homogeneously. There is another method which involves the addition of a graft monomer and a catalyst to a polyolefin suspended or dissolved in a suitable solvent. In the present invention, the grafted polyolefins to be used may be prepared by any methods.

It is preferred that the amount of the graft monomer to be incorporated into the polyolefin-containing thermoplastic organic polymer composition should be from 10^{-4} to 10% based on the total weight of the composition containing the grafted polyolefin.

In one preferred embodiment of this invention, a modified polyolefin to which a graft monomer is grafted in a high concentration is first prepared, and then this modified polyolefin is blended with a non-grafted polyolefin so that the amount of the grafted monomer contained in the mixture is 10^{-4} to 10% by weight. This is a good method of controlling the amount of the graft monomer. It is possible, however, to graft a graft monomer in the desired amount without resorting to blending.

In any case, it is necessary that the polyolefin should contain a predetermined amount of the graft monomer in a form grafted to the polyolefin (hereinafter, this graft monomer-containing polyolefin may sometimes be referred to as a modified polyolefin).

In order to achieve the objects of this invention, it is preferred to use polyolefins having maleic anhydride or acrylic acid grafted thereto. A polyolefin to which maleic acid and styrene are both grafted is also useful. The especially preferred amounts of acrylic acid, maleic anhydride, and styrene are 0.1 to 10% by weight.

A polyolefin to which both maleic acid and styrene are grafted and a method of its preparation are described in the specification of Japanese Laid-Open Patent Publication No. 1697/71.

The preferred combination of the polyolefin and the graft monomer include modified polypropylene prepared by grafting

maleic anhydride to polypropylene, and modified polyethylene prepared by grafting maleic anhydride and styrene to polyethylene.

Examples of the polyamides useful in the present invention are nylon 6, nylon 66, nylon 11, or nylon 12, preferably those having a viscosity $[230^{\circ}\text{C.}, 50 \text{ kg/cm}^2]$, measured using a FLOW TESTER (KOUKASHIKI-SHIMADZU) (0.5 mm ϕ , L/D=2) of not more than 10^4 poises. If polyamides having too high a viscosity are used, there will be a difference in optimum molding temperature between the polyamide and the modified polyolefin. Thus, if the molding temperature of the die is set to suit the polyamide, the modified polyolefin tends to be degraded at that temperature. On the other hand, if the molding temperature is set to suit the modified polyolefin, the flowability of the polyamide is low, and the molding is likely to fail.

The bottle of this invention can be produced, for example, by the conventional molding method for multilayered bottles, such as the method disclosed in Japanese Patent Publication No. 23635/69.

Also, there can be used a method wherein a plurality of orifices are provided concentrically, a plurality of tubes superposed concentrically are extruded from each of the orifices, and the tubes are bonded to each other, followed by blowing.

In an alternative embodiment, a multilayered pipe of a modified polyolefin and a polyamide is first fabricated, and after cooling reheated so as to stretch and blow mold the pipe.

In the production of the bottle of this invention, it is especially preferred that the modified polyolefin layer and the polyamide layer are taken from the extruder in a state of being coalesced within the die.

The molding temperature that is employed in the present invention should be 200 to 300°C. in the vicinity of the die. The molding fails at temperatures lower than 200°C. while temperatures above 300°C. are likely to cause the decomposition of the polymers.

In the multi-layered bottle of this invention, the thickness of the polyamide layer is preferably 1 to 50%, more preferably 10 to 20%, of the thickness of the modified polyolefin layer. If the polyamide layer is made thicker than this, the draw down of the molded article cannot be avoided, and it is difficult to mold a bottle of uniform thickness. Furthermore, because of the low viscosity of the polyamide, it is impossible to raise the blow ratio. From an economic point of view, the thickness of the polyamide layer need only be such that the resulting bottle has a sufficiently low gas-permeability.

Since the polyolefins are relatively low in cost in spite of their poor rigidity, it is economically feasible to design the die so that

the thickness of the modified polyolefin layer is rendered larger so as to maintain the mechanical strength of the blow-molded bottle, and a thin polyamide layer is laminated to the modified polyolefin layer.

In the production of the bottle of this invention by blow molding, burrs consisting of a mixture of the modified polyolefin and the polyamide are inevitably formed, and must be recovered. It is permissible if the amount of the polyamide present in the recovered burrs is less than 5% by weight. If the amount is larger, a reduction in viscosity due to poor compatibility of the polyamide with the modified polyolefin is caused to an undesirable degree. The incorporation of less than 5% by weight of the polyamide in the modified polyolefin not only does not affect the properties of the modified polyolefin adversely, but also tends to improve the adhesion between the modified polyolefin and the polyamide. If the recovery of the burrs is also taken into consideration, it is advisable to decrease the proportion of the polyamide used relative to the modified polyolefin.

In the multi-layered blow molded bottle of this invention, the inner layer may be a polyamide layer and the outer layer a modified polyolefin layer, or vice versa. A bottle consisting of three layers is also effective. It includes a sandwich structure in which a layer of a polyamide is interposed between two layers of modified polyolefin, a sandwich structure in which a layer of a modified polyolefin is interposed between two layers of a polyamide, and a three-layered structure in which a layer of a modified polyolefin is interposed between a layer of a non-modified polyolefin (the outermost or innermost layer) and a layer of a polyamide (the innermost or outermost layer). Bottles consisting of four or more layers are also possible.

As will be seen from the Examples and Comparative Examples to be described below, the present invention exhibits the following outstanding advantages.

By producing multi-layered hollow molded bottles using a polyamide layer and a layer of modified polyolefin, the defects of bottles produced separately from these materials respectively are made up, and only the merits of each of these materials are exhibited by the multi-layered bottles obtained. Furthermore, the carboxylic acid, carboxylic acid ester, carboxylic acid amide, carboxylic acid imide or carboxylic acid metal salt unit contained in the modified polyolefin increases compatibility with the polyamide and thus increases the adhesion between these two layers. In particular, by laminating a thin polyamide layer to the modified polyolefin layer, the rigidity and transparency of the polyolefin layer are increased, and its mechanical strength increased. Moreover, the difficulty of blow

molding due to the properties of the polyamide can be reduced.

Bottles of this invention in which the inner layer is a polyamide and the outer layer is a modified polyolefin are useful as receptacles for liquids consisting mainly of an organic solvent such as an aromatic compound, e.g. benzene, toluene, xylene, phenol, or styrene, gasoline, an aliphatic compound, e.g. kerosene or heavy oil. Bottles in which the inner layer is a modified polyolefin and the outer layer is a polyamide can be effectively used as receptacles for foodstuffs in aqueous solution form or wines and liquors and drinks which require resistance to permeation of gas. Bottles having a sandwich structure in which an interlayer of a polyamide is held between layers of modified polyolefin are suitable for use as receptacles for medicines which require especially superior resistance to gas permeation.

The amount of the modified polyolefin can be reduced by producing a three-layered structure in which the innermost layer is a layer of a non-modified polyolefin, the interlayer is a layer of a modified polyolefin, and the outermost layer is a layer of a polyamide. Accordingly, the cost of the material can be reduced, and the safety of the bottle for foodstuffs and medicines can be enhanced. High density polyethylene not containing a stabilizer can be used in preparing milk containers, and polypropylenes of some grades can be used in preparing containers for medicines.

In the following Examples and Comparative Examples, the properties of the bottles were measured as follows:

1. *Tensile strength*

ASTM D638—64T

2. *Melt index (MI)*

ASTM D1238—65T

3. *Adhesive strength*

Peel test. This test involves peeling off one end portion of a rectangular test piece having a size of 2.5×10 cm, and pulling it at a chuck speed of 50 mm/min. while the inter-chuck distance is maintained at 4 cm. The stress is measured by an Instron tester.

Example 1.

Three parts by weight of polypropylene (melt index 1.0) having a molecular weight of 600,000 to which 3.5% by weight of acrylic acid had been grafted were mixed and melted within an extruder with 97 parts by weight of polypropylene (melt index 0.5; Mitsui Polypro B220, registered trademark of Mitsui Petrochemical Industries, Ltd.), and the mixture was fed into a die of a blow molding machine at 210°C. Nylon 6 (viscosity 4×10^3 poises, Amiran CM 1011, registered trademark) was melted in a separate extruder, and then fed into the die at 260°C. Within the

die were provided passages for the polymers in a concentric fashion, and the modified polypropylene passed through the outside passage, and the nylon, through the inside passage. The modified polypropylene layer had an outside diameter of 80 mm, and a thickness of 0.9 mm. The nylon 6 layer had an outside diameter of 78.2 mm and a thickness of 0.1 mm. The die lip had a diameter of 20 mm, and the core had an outside diameter of 14 mm. A 500 cc. bottle having an outside diameter of 80 mm and a height of 155 mm was molded at a blow pressure of 6 kg/cm²-g. The properties of the bottle are shown in Table 1.

Example 2.

The procedure of Example 1 was repeated except that polypropylene (melt index 1.5) having grafted thereto 0.15% by weight of acrylic acid was used instead of the polypropylene mixture. The properties of the resulting bottle are shown in Table 1.

Comparative Example 1.

The procedure of Example 1 was repeated using non-modified polypropylene (Mitsui Polypro B220, registered trademark) Mitsui Petrochemical Industries, Ltd.) and nylon 6 (Admiran CM 1011, the registered trademark). The properties of the resulting bottle are shown also in Table 1.

TABLE 1

| | Example 1 | Example 2 | Comparative Example 1 |
|---|-----------|-----------|-----------------------|
| Thickness of the bottle (mm) | 1.0 | 1.0 | 1.0 |
| Thickness of the polypropylene layer (mm) | 0.9 | 0.9 | 0.9 |
| Adhesive strength Side portion (g/inch) | 500 | 1,100 | 0 |
| Weld portion of the bottom | | | |
| State of adhesion | good | good | poor |
| Buckling load (Kg)* | 40 | 40 | 30 |
| Tensile strength | | | |
| Stress at yield point (Kg/cm ²) | 240 | 240 | 220 |
| Permeation (%) of the contents of the bottle ** | | | |
| Gasoline | 0.1 | 0.1 | 50 |
| Benzene | 0.1 | 0.1 | 30 |

*The load required to collapse the bottle.

**Determined after storage for one month at 23 °C.

Example 3 and Comparative Example 2.

5 Ten parts by weight of polyethylene (Hi-zex 5202B, registered trademark) to which 4% by weight of acrylic acid had been grafted were mixed with 90 parts by weight of polyethylene (melt index 0.3, Hi-zex 5202B, trademark registered), and a bottle of 400 cc capacity

was molded in the same way as set forth in Example 1 from this mixture and nylon 6 (Admiran CM 1011, registered trademark). The results are given in Table 2. 10

The above procedure was repeated except that the grafted polyethylene was not used. The results are also shown in Table 2.

TABLE 2

| | Example 3 | Comparative Example 2 |
|---|-----------|-----------------------|
| Thickness of the bottle (mm) | 0.75 | 0.75 |
| Thickness of the polypropylene layer (mm) | 0.65 | 0.65 |
| Adhesive strength | | |
| Side portion (g/inch) | 200 | 0 |
| State of adhesion of the weld portion at the bottom | good | poor |
| Buckling load* (Kg) | 30 | 20 |
| Tensile strength | | |
| Stress at yield point (Kg/cm ²) | 230 | 200 |
| Permeability of the contents of the bottle** (%) | | |
| Gasoline | 0.1 | 60 |
| Benzene | 0.1 | 50 |

*The load required to collapse the bottle.

**Determined after storage for one month at 23°C.

Example 4.

20 Two parts by weight of polypropylene (melt index 1.0) having a molecular weight of 600,000 to which 3% by weight of maleic anhydride had been grafted were mixed and melted within an extruder with 98 parts by weight of polypropylene (melt index 0.5, Mitsui Polypro B220, registered trademark), and the mixture was fed into a die of a blow molding machine at 210°C. Nylon 6 (viscosity 4 × 10³ poises, Admiran CM 1011, registered trademark) was melted in a separated extruder, and fed into the die at 210°C. Within 25 the die were provided passages for the polymers in a concentric fashion. The modified 30

polypropylene passed through the outside passage, and the nylon, through the inside passage. The modified polypropylene layer had an outside diameter of 80 mm and a thickness of 0.9 mm, and the nylon 6 layer had an outside diameter of 78.2 mm, and a thickness of 0.1 mm. The die lip had a diameter of 20 mm, and the core had an outside diameter of 20 mm, and the core had an outside diameter of 14 mm. A bottle of 500 cc capacity having an outside diameter of 80 mm and a height of 155 mm was molded at a blow pressure of 6 kg/cm²-g. The properties of the resulting bottle are given in Table 3. 35 40

Example 5.

5 The procedure of Example 4 was repeated except that polypropylene (melt index 1.5) having a molecular weight of 500,000 to which 0.1% by weight of maleic anhydride had been grafted was used instead of the polypropylene mixture. The properties of the resulting bottle are shown in Table 3.

Comparative Example 3.

The procedure of Example 4 was repeated 10 except that the modified polypropylene was not used. The properties of the resulting bottle are shown also in Table 3.

TABLE 3

| | Example 4 | Example 5 | Comparative Example 3 |
|--|-----------|-----------|-----------------------|
| Thickness of the bottle (mm) | 1.0 | 1.0 | 1.0 |
| Thickness of the polypropylene layer (mm) | 0.9 | 0.9 | 0.9 |
| Adhesive strength | | | |
| Side portion (g/inch) | 3,000 | 5,000 | 0 |
| Weld portion at the bottom | | | |
| State of adhesion | good | good | poor |
| Buckling load* (Kg) | 40 | 40 | 30 |
| Tensile strength | | | |
| Stress at yield point (Kg/cm ²) | 230 | 250 | 220 |
| Permeability of the contents of the bottle** (%) | | | |
| Gasoline | 0.1 | 0.1 | 50 |
| Benzene | 0.1 | 0.1 | 30 |

*The load required to collapse the bottle.

**Determined after storage for one month at 23°C.

15 Example 6 and Comparative Example 4.

A 400 cc. bottle was produced by blow molding a mixture of 10 parts by weight of polyethylene (Hi-zex 5202B, registered trademark) to which 3% by weight of maleic anhydride had been grafted and 90 parts by weight of polyethylene (melt index 0.3, Hi-zex 5202B, registered trademark) and nylon 6

(Amiran CM 1011, registered trademark) in the same way as set forth in Example 4. The results are shown in Table 4.

The above procedure was repeated except that the grafted polyethylene was not used. The properties of the bottle are shown in Table 4.

25

TABLE 4

| | Example 6 | Comparative Example 4 |
|--|-----------|--------------------------|
| Thickness of the bottle (mm) | 0.75 | 0.75 |
| Thickness of the polyethylene layer (mm) | 0.65 | 0.65 |
| Adhesive strength | | |
| Side portion (g/inch) | 600 | 0 |
| State of adhesion of the weld por- tion at the bottom | good | poor |
| Buckling load* (Kg) | 30 | 20 |
| Tensile strength | | |
| Stress at yield point (Kg/cm ²) | 230 | 200 |
| Permeability of the contents of the bottle** (%) | | |
| Gasoline | 0.1 | 60 |
| Benzene | 0.1 | 50 |

*The load required to collapse the bottle.

**Determined after storage for one month at 23°C.

Example 7.

The procedure of Example 4 was repeated except that the graft monomer used for modifying polypropylene was changed as shown in Table 5, and Amiran CM 101T (viscosity

9×10^2 poises) was used as nylon 6. The adhesive strengths of the bottles obtained are shown in Table 5. Other physical properties were almost the same as the results shown in Table 3.

TABLE 5

| Graft monomers | Adhesive strength of the side portion (g/inch) |
|---------------------------|--|
| Methyl methacrylate | 100 |
| Glycidyl methacrylate | 1,000 |
| Acrylamide | 300 |
| Sodium acrylate | 100 |
| Acrylic anhydride | 100 |
| Fumaric acid | 1,500 |
| Itaconic acid | 1,000 |
| Diethyl maleate | 300 |
| Maleic acid dimethylamide | 200 |
| Maleimide | 200 |

Example 8.

Ten parts by weight of polypropylene (molecular weight 600,000, melt index 1.0) to which 3% by weight of styrene and 3% by weight of maleic anhydride had been grafted was mixed and melted within an extruder with 90 parts by weight of polypropylene (Mitsui Polypro B220, registered trademark of Mitsui Petrochemical Industries, Ltd.), and the mixture was fed into a die of a blow molding machine at 200°C. Separately, nylon 6 (Amiran CM 1011, registered trademark) was melted in another extruder, and fed into the die at 270°C.

Within the die were provided passage for the polymers concentrically. The modified polypropylene passed through the outside passage, and the nylon 6 layer passed through the inside passage. The polypropylene layer had an outside diameter of 59 cm and a thickness of 0.6 mm, and the nylon 6 layer had an outside diameter of 95 mm and a

thickness of 0.1 mm. The die lip had an inside diameter of 20 mm, and the core outside diameter was 18 mm.

A 400 cc bottle having an outside diameter of 59 mm and a height of 174 mm was produced by blow molding at a blow pressure of 6 Kg/cm²-g. The properties of the resulting bottle are shown in Table 6.

Example 9.

The procedure of Example 8 was repeated except that instead of the polypropylene mixture, polypropylene having grafted thereto 3% by weight of styrene and 3% by weight of maleic anhydride was used. The properties of the resulting bottle are shown in Table 6.

Comparative Example 5.

The procedure of Example 8 was repeated except the grafted polypropylene was not used. The properties of the resulting bottle are also shown in Table 6.

TABLE 6

| | Example 8 | Example 9 | Comparative Example 5 |
|--|-----------|-----------|-----------------------|
| Thickness of the bottle (mm) | 0.7 | 0.7 | 0.7 |
| Thickness of the nylon 6 layer (mm) | 0.1 | 0.1 | |
| Adhesive strength (g/inch) (the side portion) | 125 | 120 | 5 |
| Adhesive state of the weld part at the bottom | good | good | poor |
| Buckling strength Stress at yield point (Kg/cm ²) | 40 | 35 | 25 |
| Tensile strength Stress at yield point (Kg/cm ²) | 250 | 250 | 210 |
| Permeation of the contents of the bottle* (%) | | | |
| Gasoline | 0.1 | 0.1 | 0.1 |
| Benzene | 0.1 | 0.1 | 55 |

*Determined after storage for one month at 23 °C.

Example 10.

One part by weight of polypropylene having a molecular weight of 600,000 (melt index 1.0) to which 4% by weight of maleic anhydride was grafted was mixed and melted within an extruder with 99 parts by weight of polypropylene (Mitsui Polypro B220, melt index 0.5, registered trademark of Mitsui Petrochemical Industries, Ltd.), and the mixture was fed into a die of a blow molding machine at 210°C. Nylon 12 (Daiaamid L2121, registered trademark, melting point 178°C.) was melted in another extruder, and fed into the die at 210°C.

Within the die were provided passages for

the polymers concentrically. The nylon 12 layer passed through the outside portion of the passage, and the modified polypropylene layer through the inside portion of the passage. The nylon 12 layer had an outside diameter of 80 mm and a thickness of 0.1 mm, and the polypropylene layer had an inside diameter of 78 mm and a thickness of 0.9 mm. The die lip had a diameter of 20 mm, and the outside diameter of the core was 14 mm.

A 500 cc bottle was produced by blow molding at a blow pressure of 6 Kg/cm²-g. The properties of the resulting bottle are shown in Table 7 below.

TABLE 7

| | |
|--|-------|
| Thickness of the vessel (mm) | 1.0 |
| Thickness of the polypropylene layer (mm) | 0.9 |
| Adhesive strength (g/inch) of the side portion | 2,000 |
| Adhesive state of the weld part at the bottom | good |
| Buckling load (Kg) | 42 |
| Tensile strength | |
| Stress at yield point (Kg/cm ²) | 250 |
| Permeation of the contents of the bottle* (%) | |
| Gasoline | 0.1 |
| Benzene | 0.1 |

*Determined after storage for one month at 23°C.

Example 11 and Comparative Example 6.

5 Ten parts of polyethylene to which 5% by weight of styrene and 5% by weight of maleic anhydride had been grafted were mixed with 90 parts by weight of polyethylene. A 400 cc bottle was produced by blow molding the mixture and nylon 6 (Amiran CM 1011, regis-

tered trademark) in the same way as set forth in Example 8. The results obtained are shown in Table 8. 10

The foregoing procedure was repeated except that the grafted polyethylene was not used. The results are also shown in Table 8.

TABLE 8

| | Example 11 | Comparative Example 6 |
|--|------------|-----------------------|
| Thickness of the bottle (mm) | 0.75 | 0.75 |
| Thickness of the nylon layer (mm) | 0.10 | |
| Adhesive strength (g/inch) of the side portion | 100 | 5 |
| Adhesive state of the weld portion at the bottom | good | poor |
| Tensile strength | | |
| Stress at yield point (Kg/cm ²) | 230 | 200 |
| Buckling strength | | |
| Stress at yield point (Kg/cm ²) | 30 | 20 |
| Permeation of the contents of the bottle* (%) | | |
| Gasoline | 0.1 | 60 |
| Benzene | 0.1 | 50 |

*Determined after storage for one month at 23°C.

Example 12.

One part by weight of polypropylene having a molecular weight of 600,000 (melt index 1.0) to which 4% by weight of maleic anhydride had been grafted was mixed and melted within an extruder with 99 parts by weight of polypropylene (Mitsui Polypro B220, registered trademark of Mitsui Petrochemical Industries, Ltd.), and the mixture was fed into a die of a blow molding machine at 210°C. Separately, nylon 11 (RILSAN RESN, registered trademark, melting point 185°C.) was melted in another extruder, and fed into the die at 210°C.

Within the die were provided three flow passages concentrically. The innermost and outermost passages were used for passage of the mixture of polypropylenes described above, and the nylon 11 layer passed through the interpassage. The three layers coalesced with each other within the die or immediately after leaving the die to form a three-layered structure. The outside polypropylene layer had an outside diameter of 80 mm and a thickness of 0.45 mm, and the inside polypropylene layer had an inside diameter of 78 mm and a thickness of 0.45 mm. The nylon 11 layer

had a thickness of 0.1 mm. When the layers coalesced within the die, the lip had a diameter of 20 mm, and the core had an outside diameter of 14 mm.

A 500 cc bottle having an outside diameter of 80 mm and a height of 155 mm was produced by blow molding at a blow pressure of 6 Kg/cm²-g. The properties of the bottle are shown in Table 9.

Example 13.

One part by weight of polypropylene having a molecular weight of 600,000 (melt index 1.0) to which 4% by weight of maleic anhydride had been grafted was mixed and melted within an extruder with 99 parts of polypropylene (Mitsui Polypro B220, registered trademark, melt index 0.5), and the mixture was fed into the interlayer of a die of a blow molding machine at 210°C.

Nylon 6 (Amiran CM 1011, registered trademark, viscosity 4×10^3 poises) was melted in another extruder and fed into the outside layer of the die. Within the die were provided three flow passages concentrically. Polypropylene passed through the innermost layer, the modified polypropylene through the interlayer, and

the nylon 6 layer through the outermost layer. The three layers coalesced with each other within the die or immediately after leaving the die to form a three-layered structure. The outside nylon layer had an outside diameter of 80 mm and a thickness of 0.1, and the modified polypropylene layer had an outside diameter of 79.8 mm and a thickness of 0.1 mm. The polypropylene layer had an inside diameter of 78 mm and a thickness of 0.8 mm. When the layers coalesced within the die, the die lip had a diameter of 20 mm, and the core had an outside diameter of 14 mm.

A 500 cc bottle having an outside diameter

of 80 mm and a height of 155 mm was produced by blow molding at a blow pressure of 6 Kg/cm²-g.

Polypropylene (Mitsui Polypro B220) used as the innermost layer of this bottle passed the Testing Method for "Plastic Containers for Infusion" in accordance with the Japanese Pharmacopoeia under the administration of the Ministry of Health and Welfare, and proved suitable for use as containers for medicines.

The properties of the bottle obtained are as shown in Table 9.

TABLE 9

| | Example 12 | Example 13 |
|--|---|---|
| Thickness of the bottle (mm) | 1.0 | 1.0 |
| Thickness of the layers (innermost/inter/outermost) (mm) | modified polypropylene/nylon/modified polypropylene (=0.45/0.10/0.45) | polypropylene/modified polypropylene/nylon (=0.8/0.1/0.1) |
| Adhesive strength | | |
| Modified polypropylene/nylon (g/inch) | 2,000 | 2,000 |
| Polypropylene/modified polypropylene | — | no peel off |
| Adhesive state of the weld portion at the bottom | good | good |
| Buckling load (Kg) | 41 | 42 |
| Tensile strength | | |
| Stress at yield point (Kg/cm ²) | 250 | 250 |
| Permeability of the contents of the bottle* (%) | | |
| Gasoline | 0.1 | 0.1 |
| Benzene | 0.1 | 0.1 |

*Determined after storage for one month at 23°C.

Example 14.
Soybean oil was placed in the bottle obtained in Example 12, the bottle obtained in Example 10, and a bottle produced only from polypropylene (control), and stored for 21 days at 50°C., and the peroxide value was

examined. The results obtained are shown in Table 10. The peroxide value expresses the degree of oxidation, and is determined as follows: Potassium iodide is added to the sample, and the liberated iodine is titrated with a solution of sodium thiosulfate. The

milliequivalents of the consumed sodium thiosulfate per kilogram of the sample are determined, and taken as the peroxide value. Larger

peroxide values show larger degrees of oxidation.

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TABLE 10

| | Duration of storage (days) | Control | Example 12 | Example 10 |
|---------------------------|----------------------------|---------|------------|------------|
| Peroxide value (M-mol/Kg) | 0 | 7.6 | 7.6 | 7.6 |
| | 21 | 16.0 | 9.0 | 8.0 |

WHAT WE CLAIM IS:—

1. A multi-layered blow-molded bottle comprising at least one layer (1) of a polyamide and at least one layer (2) of a thermoplastic organic polymer composition containing a polyolefin having at least one monomer grafted thereto, the monomer being an ethylenically unsaturated carboxylic acid or an anhydride, ester, amide, imide or metal salt thereof.
2. A bottle according to claim 1, wherein the thermoplastic organic polymer composition is composed of a homopolymer of an olefin and the grafted polyolefin.
3. A bottle according to claim 1 or 2, wherein maleic anhydride is grafted onto the polyolefin.
4. A bottle according to claim 3, wherein maleic anhydride and styrene are grafted onto the polyolefin.
5. A bottle according to claim 1 or 2, wherein acrylic acid is grafted onto the polyolefin.
6. A bottle according to any one of the preceding claims, wherein the polyamide

layer (1) constitutes the inside layer of the bottle, and the layer (2) constitutes the outside layer.

7. A bottle according to any one of claims 1 to 5, wherein the polyamide layer (1) constitutes the outside layer of the bottle, and the layer (2) constitutes the inside layer of the bottle.

8. A bottle according to any one of claims 1 to 5, wherein one layer (2) is interposed between two polyamide layers (1).

9. A bottle according to any one of claims 1 to 5, wherein one polyamide layer (1) is interposed between two layers (2).

10. A bottle according to any one of claims 1 to 5, wherein one layer (2) is interposed between one polyamide layer (1) and one layer of a homopolymer of an olefin.

11. A bottle according to claim 1 substantially as hereinbefore described.

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